Arturs Laimite

SOLAR ENERGY UTILIZATION IN WATER TREATMENT

Degree Programme in Environmental Engineering

2014

samk
Satakunnan ammattikorkeakoulu
Satakunta University of Applied Sciences

SOALR ENERGY UTILIZATION IN WATER TREATMENT

Laimite, Arturs
Satakunta University of Applied Sciences
Degree Programme in Environmental Engineering
May 2014
Supervisor: Hannelius, Timo (Lecturer in Chemical Engineering)
Number of pages: 37
Appendices: 0

Keywords: water treatment, solar disinfection, UV radiation

ABSTRACT

The purpose of this thesis was to determine whether solar water disinfection can be applied in Finland and what would be the efficiency of this process. World population grows steadily and combined with increasing urbanization it causes a major stress to the natural environment. Demand for good quality drinking water increases each year, but resources of fresh water are diminishing. Nowadays most of the water purification stations are designed to use conventional, nonrenewable resources as source of energy. In order to become more sustainable, water treatment plants need to switch on more renewable energy sources. Using solar radiation as part of water disinfection process can minimize environmental effect of water treatment plants, as well as reduce operation costs. According to the results it is possible to use solar disinfection for water treatment in Finland, but desired efficiency is not met. The best results are achieved with long exposure times and increased water temperature. The highest bacteria reduction rate was 79% at the best conditions.

.

CONTENTS

1 INTRODUCTION

SODIS (Solar Water Disinfection) was invented in 1970s by Aftim Acra. SODIS is a simple method of treating biologically contaminated water for drinking purposes especially in regions with low finances and resources. UV light travels through water and destroys or inactivates harmful microorganisms. Extensive experimentation shows that SODIS may even destroy 99,999% of bacteria (Boyle et al, 2008) and between 99,9 to 99,99% of viruses (Wegelin et al, 1994). Solar intensity is depending on location, time, season, weather conditions, and other factors. Average intensity level on Earth is about 1 400 W/m^2, but the highest values can reach more than 2200 W/m^2. It is recommended that SODIS is used in latitude range from 35^oN to 35^oS, where the majority of developing areas are located, but little experimental work has been done in higher latitudes. SODIS is not an ideal water treatment technology. It has its drawbacks, such as dependency on weather and location, clarity of water and pathogens in it. But it has one major advantage, which is simplicity and economy of the method.

2 SOLAR WATER DISINFECTION

2.1 History

- First researches done on solar disinfection were in 1970s by Aftim Acra at the university in Beirut.
- At approximately the same time other scientists were analyzing the effect of UV radiation on *E. coli* in natural waters (Tyrrell, 1976) and on poliovirus (Cubbage et al, 1979). Both of these pathogens were found to be inactivated by UV radiation.
- The first workshop for scientists of solar disinfection was held in Montreal in 1988. The main objectives were to revision the research to date, to identify future research possibilities, and to develop a detailed standard set of methods for testing. The workshop also acknowledged Acra's results that 500 W/m2 in 5 hours is a good criterion for solar disinfection (Brace Research Institute, 1988).
- In 1990s flow-through systems were designed to increase volume of water treated, photo catalysts added to improve treatment were studied (Vidal and Diaz, 1999), and concentration and reflection systems were designed to increase the irradiance (Safapour and Metcalf, 1999).

2.2 Applications in Developing Areas

Transparent PET (polyethylene terephthalate) bottles are filled with water and placed into direct sunlight on roof or on SODIS table, which is made of corrugated metal sheet. Water source is typically surface water, which can contain several life threatening biological contaminants, such as *E. coli*, *Vibrio cholerae,* and *Salmonella Typimurium*. If water has high turbidity and it is not clear enough, it should be pretreated by using simple sedimentation or filtration methods. It is suggested to keep bottles in sunlight for one day if it is sunny and for two days if it is cloudy. Water can be used for consumption after exposure time is reached.

In developing countries' rural areas technology and scientific background are often quite low, so simple water treatment method is essential for ensuring quality of drinking water. In most of these developing areas water is so contaminated that improvements of SODIS can drastically improve health of the people. According to WHO (World Health Organization) contamination of water in these areas mostly comes from fecal matter, which should be reduced down to 100cfu/ml (colony forming units per milliliter) to create a huge improvement in health (WHO, 2006). According to the Swiss Federal Institute of Aquatic Science and Technology study done in Uganda percentage of children with diarrhea in a two week period dropped from 42% to 13% and school attendance increased from 43% to 78% (EAWAG, 2008).

Table 1 Impact of SODIS on diarrhea frequency in villages in Indonesia /1/

Cases of Diarhoea in the Years '02, '03, '04 (until May '04)				
	Av.Cases Diarhoea '02 (before SODIS)	Av.Cases Diarhoea '03	Av.Cases Diarhoea '04	Reduction in '04 compared to Av.of '02 and '03
Paneda Gandor Vill.	15	16	1	90 %
Ketannga Vill.	12	12	1	87 %
Sel. Ketangga Vill.	41	41	31	23 %
Pringgabaya Vill.	30	38	15	57 %
Jerowaru Vill.	60	28	14	68 %
Pengadangan Vill.	19	6	2	86 %
Gelanggang Vill.	48	28	0	100 %
Sukamulia Vill.	10	9	2	84 %
Jenggik Vill.	11	14	3	78 %
Tebaban Vill.	12	8	4	54 %
Average Reduction of Diarhoea				73 %

SODIS process is carried out in a following procedure:

1. Maximum 2 liter PET bottle is cleaned and filled with water contaminated with microorganisms. PET bottles are used because they are widely accessible, durable, inexpensive, and they do not contain or leach any harmful contaminants into water during treatment process. Glass or other plastic bottles can be used, and they need to be transparent and thin so that UV light can go through (WHO, 2007). All labels should be removed and bottles should be washed with care. In order not to damage surface cleaning with brushes is not recommended, this would decrease light ability to pass. Scratches draw bits of dirt

or microorganisms that absorb light which could be used for treatment (Hirtle, 2007).

2. Bottles are then placed in direct sunlight. Quite popular place to put them is on roofs or on SODIS table. SODIS table is made of corrugated metal sheet, which reflects light back to the bottles to have dual passage of light. According to some tests, SODIS table increases treatment process by 20 %. It is a little bit more expensive, but corrugated steel is available and inexpensive all over the world. It holds the bottles in one place so that they cannot roll of. Also its location can be changed by carrying, as a day passes by and sunlight changes its location (The Water School, 2008).
3. It is recommended to keep bottles in sun for one or two days if it is cloudy. Rainy days are not counted, but during them rainwater can be collected and used. It has been shown that on a sunny day SODIS can treat water in 3 to 5 hours (EWAG/SANDEC, 1997). But since this in many cases cannot be measured accurately, and because most of the UV radiation occurs between 10 am and 2 pm, it is safer to keep bottles out for a whole day.
4. After aforementioned procedures have been taken water can be consumed, and it has a much lower probability of causing water-borne diseases.

Because SOIDS relies on UV light penetrating ability to reach the water and microorganisms in it, water should be fairly clear. Small dirt particles can hinder treatment because they can hide pathogens that cannot be reached. If water’s turbidity is greater than 30 NTU (Nephelometric Turbidity Units) pretreatment is necessary. Pretreatment methods include sedimentation or settling, during which dirt particles will settle down, or filtration with a simple cloth or gauze. First filtration should be done and then sedimentation in a larger water tank so that suspended solids would settle on the bottom, but clear water could be drawn away (Water School, 2008).

Water that is once treated does not require to be transferred to a different water vessel before consumption. This is a significant factor of reducing water recontamination, because new vessel can contain some microorganisms and thus treatment process would be invalid, and it has to be repeated.

2.3 Solar Radiation and Its Mechanism

The UV light reaches the Earth's surface in mostly UVA and some UVB regions consisting of wavelength from 315-400 nm and 280-315 nm, respectively. UVC has the shortest wavelength (200-280 nm) and it is used as germicide to destroy microorganisms, almost all of UVC light is absorbed by the ozone layer. UV light is absorbed by DNA causing thymine bases to bond covalently forming dimers. These thymine dimers terminate the DNA replication process prematurely (Acra, 1984). Incorrect repair of thymine dimer can cause genetic mutation. The DNA absorbance of UV light is strongest in UVC region, but a sufficient dose of UVA light can still inactivate microorganisms (Setlow, 1974). DNA has its maximum absorption at 200nm and 265nm (von Sonntag, 1986). The level of disinfection is determined by the amount of radiation energy received per area [mJ/cm^2].

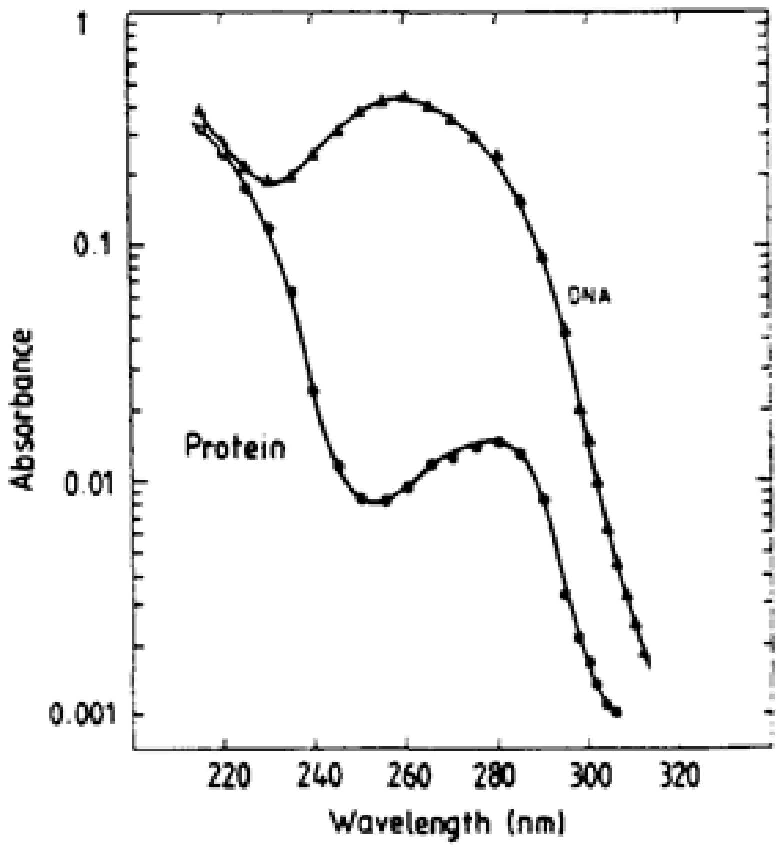


Figure 1 Absorption spectra of DNA and protein /2/

Dissolved organic matter in water absorbs UV light and by photochemical reactions highly reactive elements, such as hydroxyl radicals (OH), superoxides (O_2^-), and hydrogen peroxide (H_2O_2) are produced. These compounds oxidize cellular components of microorganisms damaging or destroying them (McGuigan et al, 1998).

Red and infrared light is absorbed by the water thus raising the water temperature. Increased heat causes denaturation, disrupting protein functions and often destroying microorganism. This heat energy has a synergistic effect with the UV mechanisms at above 45^{o}C (McGuigan et al, 1998). Temperature exceeding 50 ^{o}C decreases time required for treatment three times to have the same SODIS efficiency compared to solar disinfection at lower temperatures (Wengelin et al, 1994). Below these temperatures 3 to 5 hours of solar radiation above 500 W/m^2 is enough to provide inactivation of microorganisms (EAWAG/SANDEC, 1997).

There are still ongoing researches. It is shown that the primary damage of *E. coli* cells effect cytoplasmic membrane transport processes, although there is not much information on this transport interruption mechanism. Investigations are done to determine the way cells are altered and destroyed, including determining the ATP content of cells, traditional plating procedures, and methods that use flow-cytometer. By detecting damage at the protein, lipid, and DNA levels inactivation process will become clearer (EAWAG, 2009).

Some pathogens can encounter the effect of exposure by dark reactivation or photo reactivation. Dark reactivation happens when a microorganism's defense system finds problem in DNA sequences and repairs it. Photo reactivation happens, when low dose of UVA radiation causes the release of photolase, an enzyme that splits thymine dimers and restores organism's growth (Bolten and Cotton, 2008). It is also possible, if some coliforms of bacteria remain after treatment, that they will continue reproduction process and increase the concentration again.

Solar radiation has a long way to reach DNA of the microorganisms. Almost all UVC is filtered out by the Earth's ozone layer as well as most UVB and some UVA radiation. Lower wavelengths are absorbed more easily. It is calculated that 98,7% of UV light that travels through the atmosphere is in the range of UVA region. After that radiation must pass through clouds and pollutants in air. Some solar radiation is absorbed by bottle, water, and particles in water, such as suspended solids and dissolved inorganic compounds. It is estimated that in water with a small amounts of these contaminants sufficient UV light will only penetrate about 10cm (Kehoe et al, 2001). At each of these steps part of the UV light is absorbed according to the material's action spectrum. At the end when UV radiation reaches DNA only a fraction of the initial intensity still remains. Germicidal wavelength which is around 260nm does not have an important part in SODIS because this wavelength is mostly absorbed before it reaches DNA cells. But even when almost all UVC light is absorbed, the very small fraction that reaches cells have a significant impact because UVC has very high energy compared to UVA (Scott, 1973).

2.4 Research in Higher Latitudes

There has been little research done on SODIS applications in higher latitudes. Study made in Waterlo, Canada in latitude of 43^{o}N shows that microorganism concentrations can be reduced by 2,7 logs using SODIS in 5 hours of exposure in August and September (Hirtle, 2008). But there can be problems during winter periods, when water temperature decreases under zero degrees Celsius. There have been tests done in high altitude regions in mountainous areas which suggest that SODIS is not as effective (Oates, 2003). But there is still place for experimental work to be done in latitudes higher than 35^{o}N.

2.5 Indicators

It would be very difficult and expensive to test water for every single pathogen that is why a few indicator organisms have been chosen to ensure effective water treatment. Indicator organisms have to be selected so that they are always present, but they also must respond to the treatment as a representative of its class. But not all indicator organisms can be used for all water treatment methods, because inactivation mechanism differs from one treatment method to another. For instance, adenovirus does not respond to UV treatment, but it is very receptive to chlorination. But at the same time some organisms are very sensitive to UV irradiation, and they might show very optimistic results. So it is necessary to perform test on several indicator organisms to obtain sensible results. Various pathogens have different levels of susceptibility of UV irradiation.

Table 2 UV disinfection dose requirements for inactivation (mJ/cm^2) /3/

Pathogen	1-Log (90%)	2-Log (99%)	3-Log (99.9%)	4-Log (99.99%)
Cryptosporidium parvum	1.3	2.5	4.3	5.7
Giardia lamblia cysts	.3	.7	1.3	1.7
Vibrio cholerae	.8	1.4	2.2	2.9
Shigella dysenteriae	.5	1.2	2	3
Escherichia coli	1.5	2.8	4.1	5.6
Salmonella typhi	1.8-2.7	4.1-4.8	5.5-6.4	7.1-8.2
Shigella sonnei	3.2	4.9	6.5	8.2
Salmonella enteritidis	5	7	9	10
Hepatitis A virus	4.1-5.5	8.2-14	12.3-22	16.4-29.6
Polio type 1	4.1-6	8.7-14	14.2-23	21.5-30
Coxsackie B5 virus	6.9	13.7	20.6	30
Rotavirus SA 11	7.1-9.1	14.8-19	23-25	36

One of these organisms is *Escherichia coli*, which is the most commonly used to test for fecal contamination, because it has been intensively studied, it is well understood, and it is simple to manage (Schlosser et al, 1999). *E. coli* is a gram-negative, thermo tolerant, and anaerobic rod-shaped bacteria. Infection with *E. coli* can cause diarrhea and abdominal cramping, sometimes nausea, chills, loss of appetite, headache, and muscle cramps. Illness develops in 1 to 3 days and usually lasts for 3 to 4 days. Infection can occur by eating or drinking foods that are contaminated with *E. coli* bacteria, but the biggest source of contamination is from human or animal feces. World Health Organization has set recommendations stating that there should be 0 *E. coli* and 0 thermo tolerant coliforms in 100 ml of drinking water (WHO, 2013). *E. coli* is very sensitive to UV treatment descending for 3 logs in 5 hours of exposure of 2000 kJ/m^2, which is dominant inactivation mechanism in SODIS treatment.

2.6 Inactivation of Pathogens

There have been several researches done on microorganism response to SODIS treatment method. *Shigella dysenteriae*, which is responsible for recovery of dysentery in large areas of the world, responds very well to SODIS, and it can be inactivated at low exposure time (Kehoe et al, 2004). *Vibrio cholera*, which is responsible for cholera, can be inactivated even better than *E. coli* (Barney et al, 2006). *Salmonella Typhimurium*, which causes salmonella, can be inactivated by 4 logs in just 5 hours (Kramer and Ames, 1987). Cryptosporidium parvum oocysts, responsible for gastro-intestinal disease cryptosporidiosis, and Giardia cysts, responsible for gastrointestinal disease giardiasis, can be inactivated in 10 and 4 hours of treatment, respectively (McGuigan et al, 1998). *Streptococcus faecalis* can be inactivated up to 6 logs in less than 3 hours (Reed, 1997).

Viruses do not respond less positively to SODIS treatment than bacteria and protozoa. Wild coliphage, virus that infects *E. coli*, was reduced by just 1 log in 10 hours (Dejung et al, 2007). F2 coliphages were reduced by 2 logs in 10 hours (Wagelin et al, 1994). T2 coliphages were reduced by 2 logs just in 3 hours, when treated in a special reflective reactor (Safapour and Metcalf, 1999). Poliovirus responded minimally to SODIS at 25 ^{o}C, but when temperature is over 40 ^{o}C, it was inactivated much more effectively (Heaselgrave et al, 2006). This kind of phenomenon or synergy between SODIS and elevated water temperature has been observed for several pathogens.

3 FACTORS INFLUENCING ON SOLAR DISINFECTION

3.1 Temperature

As stated in previous chapters, elevated temperature has an impact on water treatment rate. Water temperatures of 45-50 ^{o}C increase inactivation rate and cause more rapid treatment, which can be increased by up to three times. When microorganisms are surrounded by high temperature they are more vulnerable and acceptable of UV irradiation, so it can do more damage and destroy cells more rapidly. Reflectors and mirrors can be used to increase water temperature (Wagelin et al. 1994).

3.2 pH

There is a connection between lower pH values and increased microorganism inactivation rates. A series of experiments showed that there is a relation between low pH and increased inactivation rates of *E. coli* in sunlight, but no significant inactivation in the dark. Low pH values might increase stress to the microorganism cells, for example by requiring it to spend more energy on maintaining pH at a constant level, thus accelerating depletion of energy resources. This stress might reduce the rate at which energy-consuming proteins can repair damaged DNA cells. The most dramatic effects can be observed at pH 3. Increased inactivation can be observed when pH is gradually reduced from 7 to 4 (Rincon and Pulgarin, 2004). Although there is a relation between pH and inactivation rates, in many cases it is too difficult to adjust pH at proper level for household applications, but it might be feasible for larger units.

3.3 Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a widely used disinfectant and is used in water treatment. Hydrogen peroxide is a strong oxidizer. Amount of 500 mM hydrogen peroxide, i.e. 17 g H2O2 per liter, approximately doubles the inactivation rate, and it decreases in the presence of *E. coli*. Field trials have shown success in accelerated *E.*

coli and total coliform inactivation. In Haiti, increased hydrogen peroxide led to faster inactivation of *E. coli* and total coliforms, compared to control samples without added hydrogen peroxide. Amount of 500 mM hydrogen peroxide was added. Inactivation rates are dramatically increased when water temperature reaches 35 ^{o}C and adding 100 mM hydrogen peroxide, but there is no effect observed in the dark. At 45 ^{o}C, there occurs inactivation in the dark and inactivation in the light is even greater with hydrogen peroxide concentrations of 100 and 1000 mM (Seaver and Imlay, 2001).

There is a human health effects that must be considered, when using hydrogen peroxide. At the moment there is no detailed information available on long-term effects of consuming low levels (max 1000 mM) of hydrogen peroxide, but information available suggests that there is no need for concern. Hydrogen peroxide has been approved for use at concentrations up to 30 mg/l or 880 mM, and it used as a drinking water additive in Europe (Weiner et al, 2001). Even though hydrogen peroxide is safe, there might be complication because of some of the stabilizers used in commercially available hydrogen peroxides. Preparation of hydrogen peroxide might include toxic additives, such as acetanilide, which is harmful for humans (CSTEE, 2001).

3.4 Copper and Ascorbate

A combination of dissolved copper sulfate and ascorbate was found to increase the inactivation rate. In the presence of 25 mM ascorbate, increasing copper concentration from 0,1 mM to 2,5 mM, raises the inactivation rate value from 0,9 to 5,3 in one hour. In the presence of 2,5mM copper sulfate, increasing ascorbate from 0 to 37,5 mM raises inactivation rate value from 3,2 to 11,3 in one hour. The copper and ascorbate mixture is also fairly effective in inactivating *E. coli* in the absence of light. $CuSO_4$ appears to have a slight improving effect on inactivation even in the absence of ascorbate. But the best results are achieved by adding 2,5 mM copper and 0-37,5 mM ascorbate (Fisher et al, 2008).

By adding four 2,5 cm long 18-gauge copper wires and 200 mM ascorbate to 100 ml of water 3 log inactivation of *E. coli* can be reached in 15 minutes. Aqueous copper concentrations steadily increase during the experiment to approximately 8 mM in 2 hours. There is no such increase of concentrations observed in the dark (Fisher et al, 2008).

By combining hydrogen peroxide, copper sulfate (2,5 mM), and ascorbate (25 mM) inactivation rate value increases. Cupper and ascorbate magnifies the effect of added hydrogen peroxide 28 times. Also significant inactivation in dark is observed, but the value reached in the presence of light is dramatically higher. Copper, ascorbate, and small amounts of hydrogen peroxide could provide extra disinfecting capacity of SODIS on sunny days as well as substitute technique on cloudy days (Fisher et al, 2008).

Available information on health suggests that these additives should be safe for consumption at concentrations that greatly improve SODIS. Copper is efficiently chelated and segregated in the human body, and no effect was observed when copper and ascorbate was fed to mice (Sagripanti et al, 1997).

3.5 Titanium Dioxide

Titanium dioxide (TiO_2) is a metal oxide which has properties like: biological and chemical stability, no toxicity, and low price. It has been found that titanium dioxide in combination with nitrogen ions or metal oxide like tungsten trioxide, is a very strong photocatalyst in UV or visible light. The strong oxidative potential oxidates water to form hydroxyl radicals, which can effectively destroy organic materials and microorganisms (Kurtoglu, Longenbach, Gogotsi, 2011).

In experiment conducted by Zizi Yu and Deborah Day, bacterial concentrations in water decreased considerably when titanium oxide was added. After 3 hours bacterial concentration had decreased below half of the original value, while control sample showed value of 63% of original. After 6 hours of exposure to light water with titanium dioxide had bacterial concentration of less than 6%, when control sample had bacterial concentration of 30%. It is evident that adding titanium dioxide in treated water increases bacteria reduction (Yu, Day, and Ciston, 2008).

It is possible to combine titanium dioxide with single-welled carbon nanotubes (SWCNT) providing a larger surface area and entrapping electrons transferred from titanium dioxide for further improvement of oxidization and bacterial reduction. In this case, direct sunlight is not necessary, but higher temperatures help to improve disinfection. Titanium dioxide and single-welled carbon nanotube combination prevents microorganism incubation and continually destroying pathogens even when temperatures are optimal for bacterial growth. Titanium dioxide and single-welled carbon nanotube combination present a more durable coating compared to just titanium dioxide, which allows a better and long lasting treatment (Yu, Day, and Ciston, 2008).

In study conducted by Dillert et al. in Hannover, Germany, they demonstrated that the titanium dioxide photocatalysis treatment of *E. coli* in pretreated wastewater is feasible disinfection method that allows municipal wastewater to be reused (Dillert et al, 1998). In similar experiment done by Herrera and his co-workers, they proved that titanium dioxide can be used for municipal wastewater to inactivate coliforms and *Streptococcus faecalis* using UV-lamps and solar light, but their experiment was limited by low levels of radiation (Herrera et al, 2000). Rincon and Pulgarin investigated *Escherichia coli* and *Enterococcus* species in wastewater from biological wastewater treatment plant in Lausanne, Switzerland. They concluded the *Enterococcus* species are less sensitive to photocatalytic treatment compared to *coliforms* and Gram-negative bacteria (Rincon and Pulgarin, 2005).

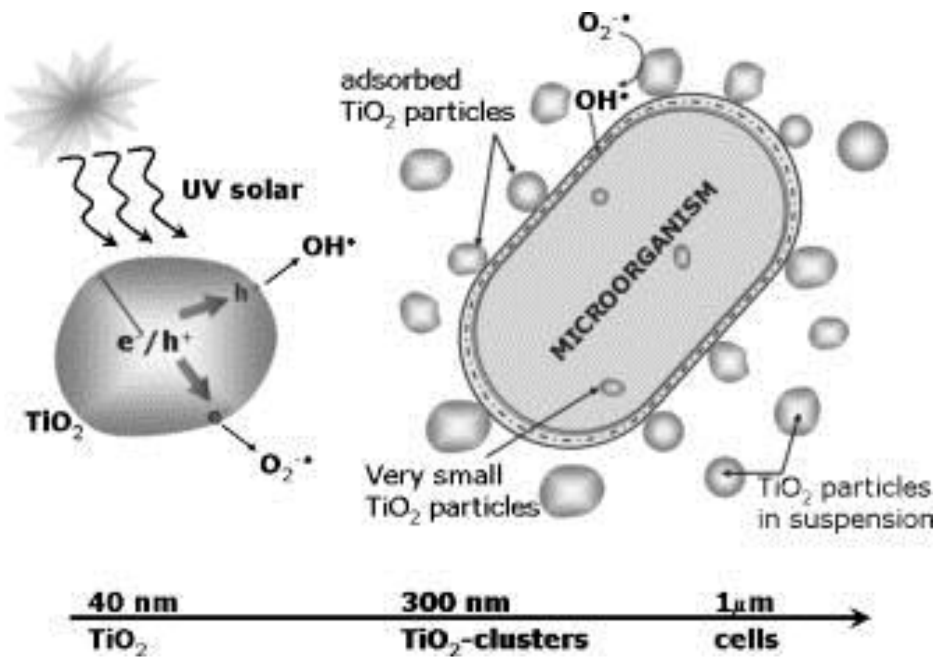


Figure 2 Mechanism of effect of titanium dioxide on microorganism in presence of UV radiation /4/

There have been several studies dealing with optimal concentration of titanium dioxide in wastewater, and suggested values range from 0,01 to 1 g/liter. Most widely used is titania Degussa P25, which is known to be most efficient of titanium dioxide.

3.6 Photo-Fenton Technology

Photo-Fenton process is the most applied method of advanced oxidizing processes (AOP) for wastewater treatment (Suty et al, 2004). The first works on the application of photo-Fenton technology for wastewater treatment were done in 1990s. In photo-Fenton process iron containing solutions are used as catalysts to improve UV-induced degradation. Many other reactions occur resulting in degradation of organic water compounds. Researches done in photo-Fenton process are mostly concentrated on fact that it should be driven by solar radiation, that is why photo-Fenton process is the most relevant of all advanced oxidizing processes. This technology has several advantages compared to classical Fenton-reaction:

- Degradation is many times higher,
- Operational costs are significantly lower since chemical consumption is lower,
- Irrelevant sludge is produced causing no problems of its removal (Website of Enviolet, 2013).

pH is an important factor in the efficiency of photo-Fenton reaction, and optimum pH is around 2,8 (Pignatello, 1992). At this pH level precipitation does not occur and the dominant iron species in liquid is $Fe(OH)^{2+}$, which is the most photoreactive ferric iron-water compound. Carboxylic acids are produced as intermediate products in an oxidative treatment. These ferric iron-carboxylate compounds have higher quantum yields than ferric iron-water compounds. Typically reaction shows an initial lag phase until these carboxylic acids are formed. They can regenerate ferrous [Fe(II), Fe2+] iron into ferric [Fe(III), Fe3+] iron more efficiently, thus accelerating the process. Ferric compounds are present in slightly acidic solution, and they absorb light in UV and visible light spectrum. The quantum yield for ferrous iron formation depends in the light wavelength, which is 0,14-0,19 at 313 nm and 0,017 at 360 nm (Faust and Hoigne, 1990).

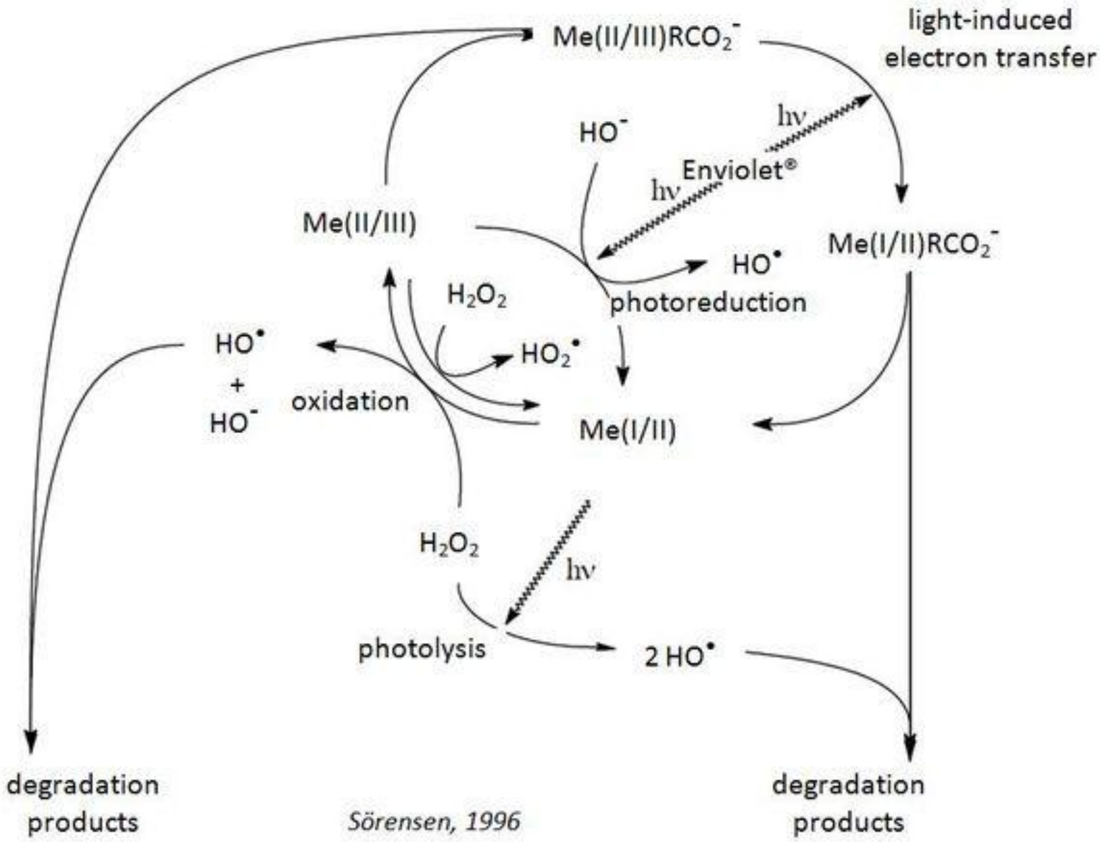


Figure 3 Photo-Fenton schema according to Sorensen (1996) /5/

Hydroxyl radicals (OH) are the main oxidizing agents responsible for photo oxidation of the majority of organic compounds studied. Hydroxyl radicals have very high oxidation potential E_o=2,8 V, while oxidation capacities for ozone, hydrogen peroxide, and chlorine are E_o=2,07 V, E_o=1,78 V, and E_o=1,36 V, respectively. First generation of electron-hole pairs occur. They are separated with conduction and valance bands. It is important to minimize electron-hole recombination by maximizing the rate of interfacial electron transfer to capture the photo generated electron or hole. This will ensure higher efficiency of photocatalytic oxidative degradation. Oxygen and water are essential for photo oxidation with TiO_2, and there is no degradation in absence of either of substances. Oxidative species react with majority of organic materials. For example, in aromatic compounds, the aromatic part is hydroxylated and oxidized leading to ring opening. The resulting aldehydes and carboxylic acids are decarboxylated to produce CO_2.

3.7 Solar Photocatalysis Degradation Process

Photocatalysis objective is to mineralize contaminants into carbon dioxide, water, and inorganics. So far, heterogeneous titanium dioxide photocatalysis and homogeneous photo-Fenton method have been studied extensively. Industrial waste water treatment has the highest perspective in using these technologies. But unluckily, there is not one certain rule and every situation is different. This treatment method has showed promise in degrading hazardous pollutants at medium or low concentrations. Transformation of mother compound is necessary to eliminate toxicity and perseverance (Malato et al, 2003). Treatment process becomes more complicated, when concentrations and amounts of contaminants increase. Problems, such as, low kinetics, low photoefficiency, and unpredictable mechanisms, arise.

Contaminants that can be treated are: alkanes, halo alkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides, phenols, agrochemical wastes, halogenated hydrocarbons, industrial pharmaceutical biocides, wood preserving waste, hazardous metal ions, cyanides, and dyes. So far, only s-triazine herbicide degradation has displayed to be unsuccessful, because the strong stability of triazine nucleus (Watanabe et al, 2005). Chlorinated molecules are released into solution. Molecules containing nitrogen are mineralized mostly to NO^{3-} and NH^{4+} (Augugliaro et al, 2002). Organophosphorous contaminants produce phosphate ions. In photo-Fenton technology phosphate cloisters iron forming non soluble salt and reduces reaction rate. More iron is needed when water containing phosphates is treated by photo-Fenton technology (Rabindranathan et al, 2003). Aromatic ring is disintegrated into organic acids and other hydroxylated compounds, and this mineralization takes more time than for other contaminants (Sarria et al, 2004). There is also increasing amounts of surfactants, pharmaceuticals, and personal care products in wastewater, which have not been thoroughly studied at the moment, but quite a lot of research is focused on these emerging contaminants.

Right now there are four general research and development directions: modifying catalysts, finding new catalysts, increasing solar photocatalytic rate, and combination with biological treatment. One way how to improve catalyst is by enlarging specific surface area (Hermann et al, 2002). Another way is to extend the spectral range of titanium dioxide into the visible light region. It can be done by adding various transition metal cations, such as Chromium, Vanadium, and Copper. So far doping with these metals have showed both positive and negative effects on photocatalytic activity of titanium dioxide. Results are inconclusive and require more studies (Sano et al, 2004). There is a lot of promise seen in photocatalysis combination with biological treatment. Biological treatment is cheap and it is the most environmentally friendly water purification process. Therefore, biologically unmanageable substances could be treated with photocatalytic technologies first, until biodegradability is achieved and water can be treated in biological treatment reservoirs. This combination reduces treatment time and optimizes process, because solar treatment system can be much smaller. The feasibility of photocatalytic and biological process combination must be considered, and it could have a significant cost reduction because of the smaller solar collector area required. Photocatalysis process can be improved by efficient measurement and control procedure. At the moment, most widely applied control system is by using toxicity testing in treated water to see degradation of microorganisms and other pollutants (Hincapie et al, 2005).

4 SOLAR COLLECTOR

Solar photocatalytic process uses high-energy short-wavelength photons to enhance photochemical reactions. The equipment required for solar photochemical applications has several common features with equipment used for heat generation. Photochemical systems and reactors have been made from conventional solar thermal collector designs, such as parabolic troughs and nonconcentrating collectors. But there are some differences between these systems. Fluid must be directly exposed to sunlight so absorber must be transparent to the photons, and temperature mostly is not a significant factor so there is no need for insulation.

4.1 Nonconcentrating Solar Collectors

Nonconcentrating solar collectors are usually static flat-plate panels aligned to the equator at specific inclination, which depends on the latitude where panel is located. Main advantages are simplicity, low manufacturing costs, easy and cheap installation, can use diffused light, and they are much better adapted for a small scale operations. But their efficiency is lower because their orientation is fixed to one path of incoming radiation. This system requires much higher photoreactor surface area, so it must support high operating pressures to pump the liquid. Despite the fact that nonconcentrating flat reactors have several advantages compared to concentrating systems, their design is unsatisfactory because of the requirements for protection against weather (Bahnemann, 2000). Photoreactors different from tubular shape have genuine disadvantages when designing them for industrial systems.

4.2 Compound Parabolic Concentrators

Compound Parabolic Concentrators (CPC) are low concentration collectors used in thermal applications. Compound parabolic concentrators merge characteristics and advantages of parabolic concentrators and static flat systems. Various research groups have found them to be a good option for solar photochemical applications. Advantages of compound parabolic concentration system are: turbulent flow conditions, absence of vaporization of volatile compounds, absence of tracking, absence of overheating, potential to use both direct and diffuse solar radiation, low cost, weatherproof properties, absence of reactant contamination, and high optical and quantum efficiency. They can use direct and diffused solar radiation. Having all these advantages compound parabolic concentration systems is one of the best options for solar photocatalytic method (Ajona and Vidal, 2000).

The main characteristics of designing solar collector for photocatalytic process are: collection of UV radiation, working temperatures should be close to surrounding temperature, and quantum efficiency. Construction and installation should be economical and efficient, with low pressure drop. Tubular reactors have crucial advantage – structural efficiency of tubing. The tubing is available in large range of different materials and shapes. One of the most important factors for photoreactor is its diameter. It is important to maintain a uniform flow in order to have high efficiency, since uniform flow causes uniform exposure time.

4.3 Solar Reactor Materials

The original solar photoreactor designs are based on parabolic-trough concentrators (PTC). Parabolic-trough concentrator technology has been fairly well developed and the existing devices could be modified for photochemical processes. Main disadvantages are: collectors use only direct radiation, costliness, and low optical efficiencies.

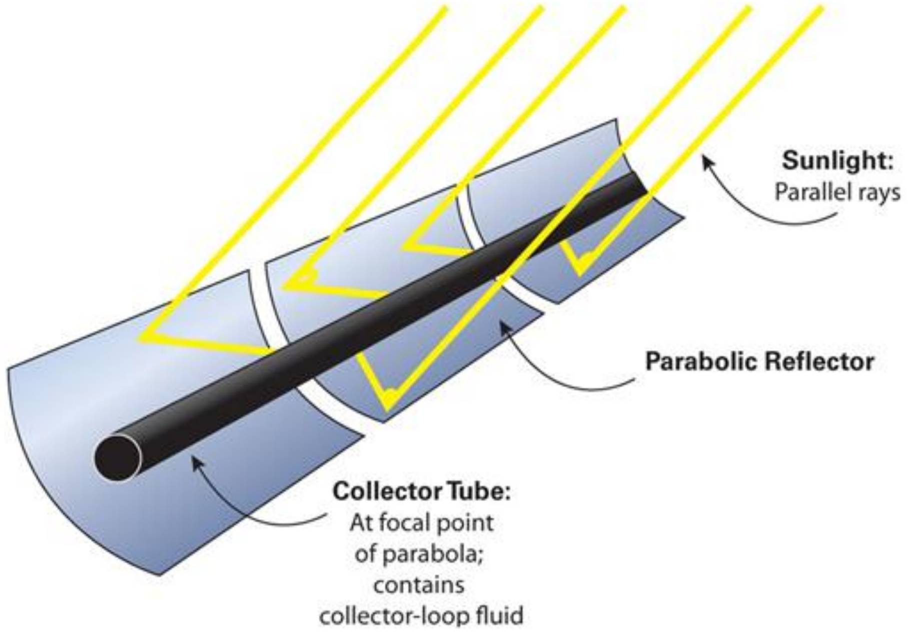


Figure 4 Parabolic-trough concentrator /6/

Equipment used for solar water treatment systems is similar and quite common in other water treatment methods. Most of the piping can be made from polyethylene or polypropylene. Metallic compounds should be avoided because they can be degraded in time by oxidation. Materials used for construction must not be reactive, and they cannot interfere with the photocatalytic process. All materials used must be inert to degradation of UV radiation in order to satisfy required lifetime of the system. Reactor must be transparent to UV radiation and it should transmit UV light efficiently and not slow it down or absorb it.

For light reflecting purposes, it is suggested to use aluminium because it has low costs and high reflectivity. Aluminium coated surface is the only metal surface that is highly reflective throughout the ultraviolet spectrum. For aluminium, the reflectivity ranges from 92,3% at 280 nm to 92,5% at 385 nm, but for silver these values are 25,3% and 92,8, respectively (Blanco and Malato, 2003).

The choice of materials that are transmissive to UV light and resistant to its effects is limited. Materials that meet these requirements are: fluoropolymers, acrylic polymers, and several types of glass. Quartz has excellent UV transmission, good temperature and chemical resistance, but it is quite expansive. Fluoropolymers can be used as source of plastic for reactors because of their good UV transmittance, UV stability, and chemical inertness. But their greatest disadvantage is that wall thickness must be increased to meet pressure resistance levels, which lowers its UV transmittance. Acrylics could also be used, but they are fragile and can disintegrate easily. Regular glass is not suitable because it absorbs part of the UV radiation due to iron inside the glass. Borosilicate glass has good transmissive properties with a cutoff of about 285nm (Blanco et al. 2000). Low iron glass would be the most suitable solution.

4.4 Installed Solar Photocatalytic Treatment Plants

There has been very little commercial or industrial use of photocatalysis as treatment method. In 1998, Dillert and his co-workers designed a laboratory and pilot plant reactor to treat biologically pretreated industrial wastewater from Volkswagen AG factories in Wolfsburg, Germany and Taubate, Brazil. They used double skin sheet reactor (DSSR), which is operated in batch mode, with total irradiated area of 27,6 m^2. The amount of 500 liters of water came from the biological treatment plant and it was pumped into the tank and mixed with titanium dioxide catalyst. This suspension was rotated between the tank and solar panel for 8 to 11 hours during daytime. After that suspension was pumped out of reactor into the tank, where photocatalyst was allowed to settle down during the night. After this sedimentation time, liquid was pumped out and new wastewater was pumped in to start treatment from beginning. More than 50% of organic pollutants were degraded in 8 to 11 hours (Dillert et al, 1999).

In 1997, Freudenhammer and his team conducted a study using thin film fixed bed reactor (TFFBR) in several Mediterranean countries. Later on pilot plant was built at site of a textile factory in Menzel Temime, Tunisia. Pilot plant consisted of two 2,5 meter wide 10 meter long reactors, with total irradiated area of 50 m^2, which was turned to the south at an angle of 20 degrees and it was installed on concrete. This plant could be operated in parallel or cascade flow in continuous recycling mode depending on kinetics. Pumps were designed for a maximum capacity of 3m^3 per hour. Two sequencing batch reactors with a total volume of 30 m^3 and a membrane aeration system were connected to the reactor for biological pre- and post-treatment (Bousselmi et al, 2004).

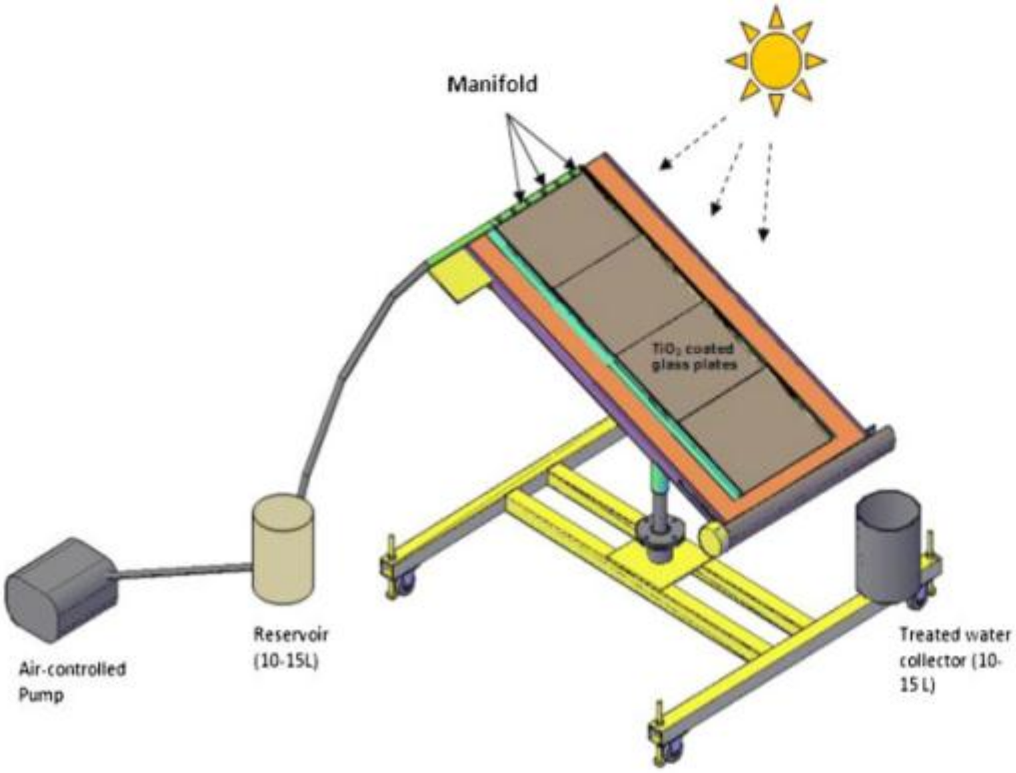


Figure 5 Thin-film fixed-bed reactor (TFFBD) /7/

In 1999, nonconcentrating solar detoxification plant using the compound parabolic collector technology was built in facilities of HIDROCEN in Madrid, Spain. This was done as a part of “Solar Detoxification Technology for the Treatment of Industrial Non-Biodegradable Persistent Chlorinated Water Chemicals” (SOLARDETOX) project to test for pre- and post- processing requirements, potential operating problems, capital and operating costs. Similar systems have been used by other researcher for treating paper mill effluents in Brazil and Germany (Sattler et al, 2004).

In 2004, compound parabolic collector based plant was installed for greenhouse agriculture pesticide container treatment in Almeria, Spain. Treatment method is based on photo-Fenton reaction, which mineralizes about 95 % of contaminants, the rest 5 % are removed by activated carbon. Process is carried out in a batch mode. The plant has 4 parallel rows of 14 photocatalytic reactor modules, which has 20 tubes per module and the area of module is 2,7m^2. Modules are connected in series so water flows from one module to another. System is mounted on a 37 degrees inclined platform. Total collector surface area is 150 m^2, and total reactor volume is 1061 liters. Before water enters the system solids are extracted and hydrogen peroxide and ferrous iron are introduced. Operating conditions for total organic carbon (TOC) of 100 mg/l are: 55 mg/l ferrous iron, from 500 to 800 mg/l hydrogen peroxide, and pH around 2,8 to avoid iron precipitation. Bach mode can treat from 1500 to 2000 liters with a treatment time of 8 to 10 hours of exposure to light. About 75% of volume is continuously exposed to the sunlight (Rossetti et al, 2004).

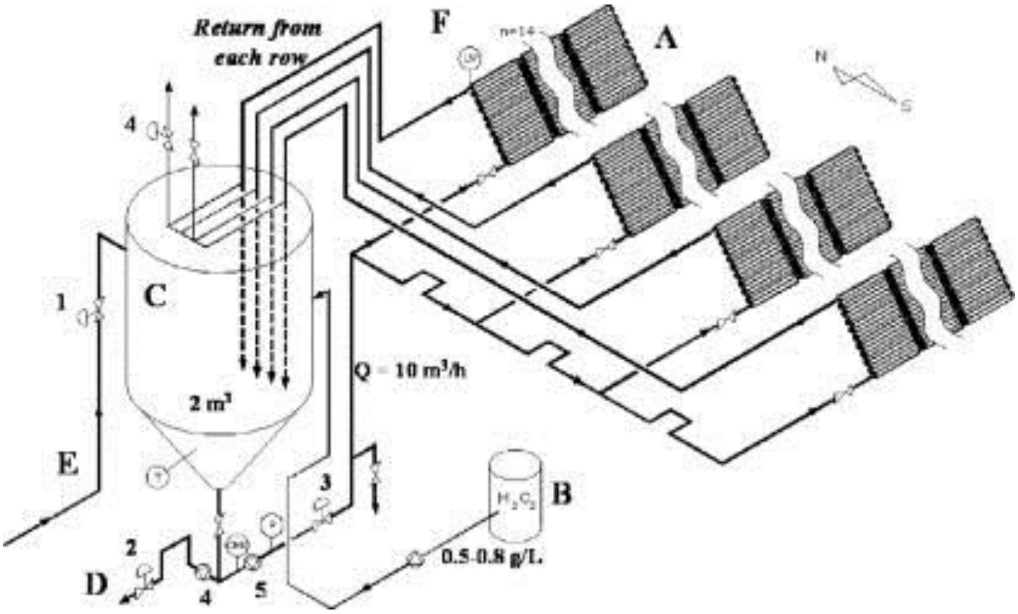


Figure 6 Schematic representation of water treatment plant in Almeria, Spain /8/

5 EXPERIMENTAL PART

5.1 Method

For practical part it was decided to expose water from river Kokemäenjoki for solar irradiance and measure how does UV radiation affect pathogens in water. There are two major scenarios in which this part can be divided in. In the first scenario, water is subjected to artificial UV radiation generated from UV lamp in laboratory environment. This experimentation part is held indoors. For the second scenario water is subjected to natural solar light and UV radiation outdoors. Sky in Finland is quite often covered by clouds, which makes experimentation outside worthless in a cloudy day, because very little UV radiation can reach water making treatment impossible, but test can be done to specify if some inactivation happens also in clouded conditions. The water tank is the same for all situations. Its dimensions are 0,29 m * 0,37 m * 0,25 m. So it can be compared to nonconcentrating solar collector. Water is filled to 0,1 and 0,05 m marks for different water thickness. Volume of the water is 10,7 and 5,4 liters, respectively. Pathogens tested for water contamination are *E. coli*. Samples are taken before treatment begins and after treatment and put into petri dishes for bacteria incubation. After two days of incubation amount of visible bacteria is counted and compared to initial bacteria amounts. From these results we can see how effective is treatment and what parameters should be changed.

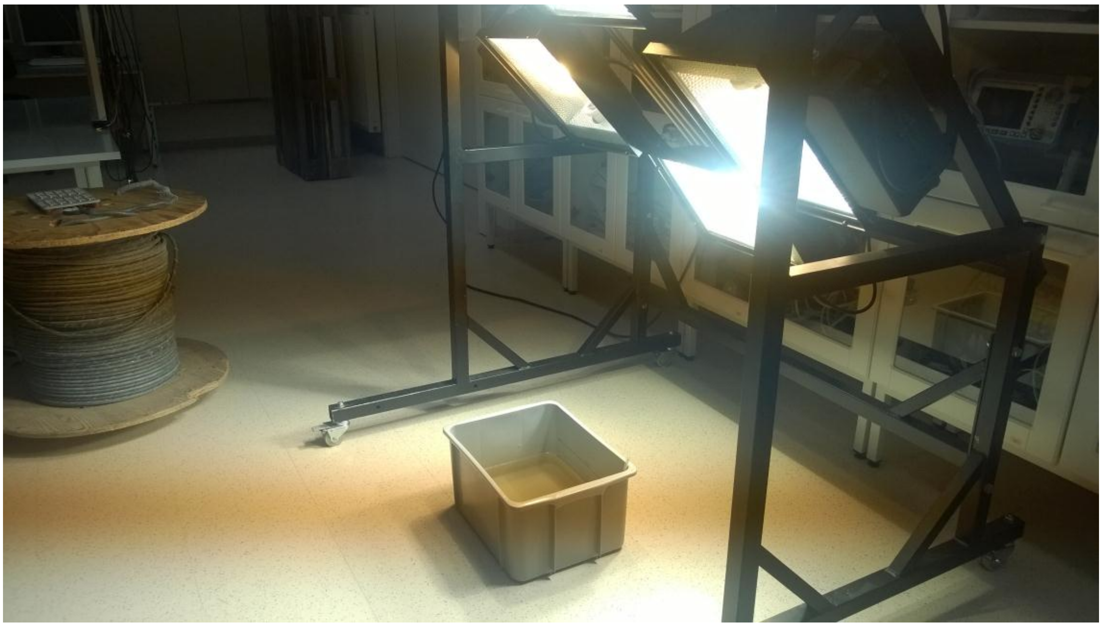
Different parameters that can be changed are:

- Initial Water temperature (20 ^{o}C or 40 ^{o}C),
- Reflective layer on bottom of the water tank,
- Water depth (0,1 or 0,05 meters), and
- Irradiance time (3, 6, or 8 hours).

5.2 Results

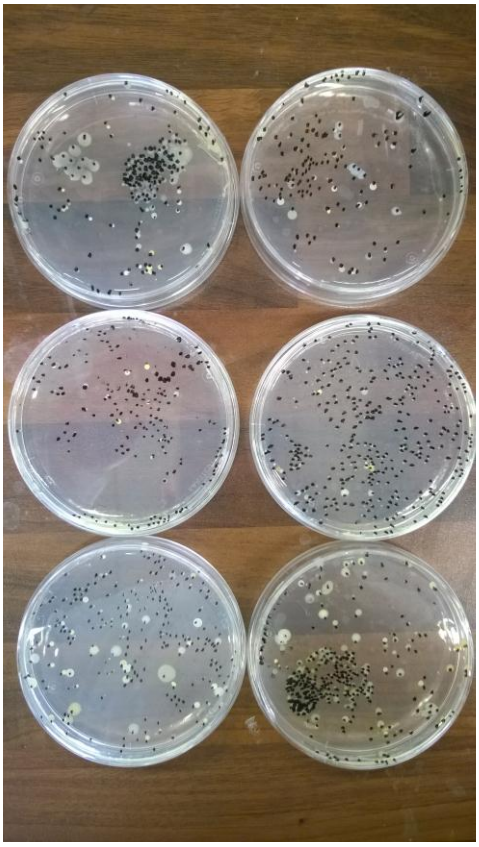
5.2.1 Treatment with UV Lamp

Results for water treated by lamps are summarized below. Irradiance time for samples was 3 and 6 hours, water depth 0,05 m, average UV-A radiation 3,4 W/m^2, average UV-B radiation $10,7*10^{-3}$ W/m^2, and water temperature ranged from 21 ^oC at the beginning of experiment to 26 ^oC, when experiment was concluded.



Picture 1 Experimental procedure in laboratory.

After two days of incubation at 30 ^oC temperature, results were gathered in table 4. In picture 2 on the top are samples with 6 hours of irradiance, in the middle with 3 hours, and on the bottom initial water. Coliforms are highlighted with black marker.



Picture 2 Petri dishes with coliforms.

Table 3 Reduction of coliforms in different time intervals under UV lamp.

	Average amount of coliforms	Reduction
Initial	287	0%
After 3 hours	280	2,5%
After 6 hours	167	42%

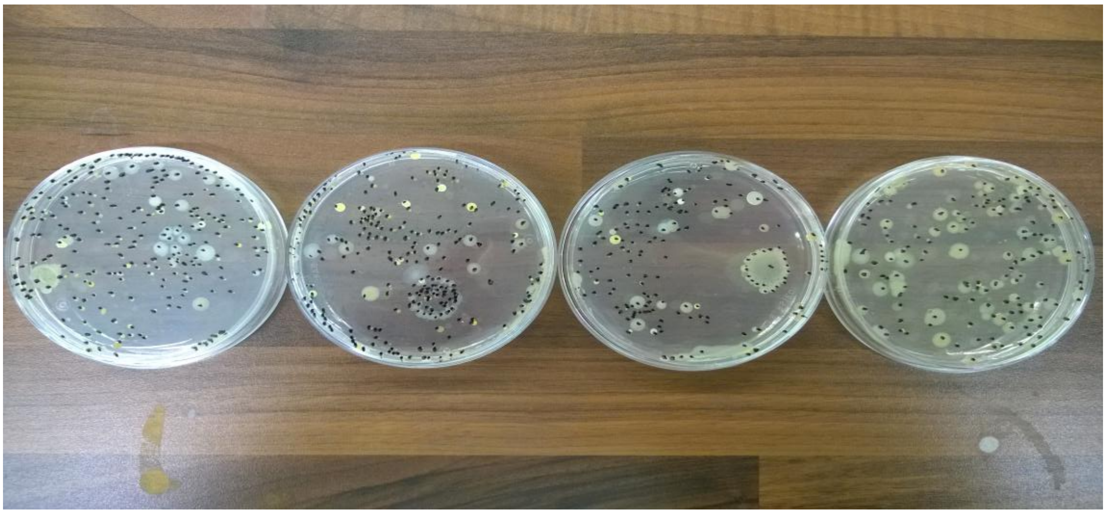
It is evident that irradiation time is a major factor in reduction of bacteria. If after 3 hours there is nearly any reduction, then already after 6 hours almost half of the bacterial population is destroyed.

5.2.2 Treatment with Sun Radiation

Irradiance time for samples was 3, 6, and 8 hours, water depth 0,05 m. UV-A radiation at 2 pm was 10,54 W/m^2, UV-B radiation at 2 pm was 528*10^{-3} W/m^2, both of these values are higher than what we got for under-the-lamp measurements. Sky was clear during whole experiment time. Air temperature increased from 6 ^{o}C at 8:30, when experiment was started, to 16 ^{o}C at its highest at 2 pm. Water temperature initially was 20 ^{o}C and it decreased to 18 ^{o}C during the course of experiment. Results for water treated under direct sunlight are summarized below.

Picture 3 Implementation of experiment under direct sunlight.

It is seen that some places were covered in shade for some time of experiment.



Picture 4 Petri dishes with coliforms.

It is clearly visible that reduction after just three hours is very small, but after six and eight hours it is much higher. We can see that amount of bacteria has decreased in time in picture 4. From left to right initial water sample, water after 3 hours of exposure, water after 6 hours, and water after 8 hours

Table 4 Reduction of coliforms in different time intervals under sun radiation

	Average coliform amount	Reduction
Initial	246	0%
After 3 hours	235	4,5%
After 6 hours	168	31,7%
After 8 hours	139	43,5%

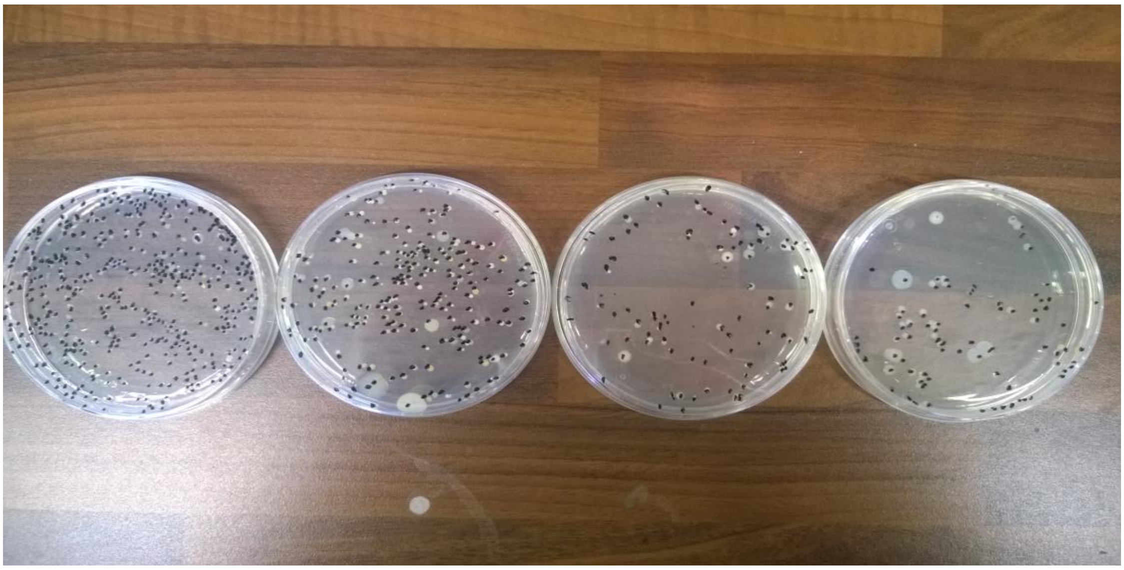
From the table above it is visible that increased irradiation time increases reduction rate. The same result what was achieved from under-the-lamp measurement. Reduction after 6 hours is less compared to previous experiment. Reduction after 8 hours is slightly higher. We can deduce that, although UV-A and UV-B radiation measurements showed higher values compared to laboratory conditions, UV radiation outside is no as uniform and constant during long periods of time. That explains why reduction rate outside is smaller.

5.2.3 Treatment with Sun Radiation and Increased Temperature

In this experiment water depth was changed form 0,05 m to 0,1 m. Irradiance time for samples was 3, 6, and 8 hours. UV-A radiation at 2 pm was 11,7 W/m^2, UV-B radiation at 2 pm was $721*10^{-3}$ W/m^2, both of these values are higher than previous values for under-the-lamp measurements. Sky was clear most of the day, but between 1 pm to 3 pm it was partly cloudy. Air temperature increased from 20 ^oC at 9 am, when experiment was started, to 28 ^oC at its highest at 2 pm. Water temperature initially was 20 ^oC and it increased to 35 ^oC during the course of experiment. Results for water treated under direct sunlight are summarized below.

Table 5 Reduction of coliforms in different time intervals

	Average coliform amount	Reduction
Initial	399	0%
After 3 hours	314	21,3%
After 6 hours	121	69,7%
After 8 hours	80	79,9%



Picture 5 Petri dishes with coliforms at different exposure times.

Reduction of amount of bacteria in water samples can be seen in picture 5. From left to right initial water sample, water after 3 hours of exposure, water after 6 hours, and water after 8 hours. It is evident that increased temperature has a dramatic effect on bacteria reduction. Even after just three hours of exposure bacteria amount had decreased by more than 20%, which is much more compared to previous experiments. Although water level was twice as high as in previous experiments, it had little effect on reduction rate. This is the best achieved result so far, and reduction rate increased as high as 80%, which is already a significant decrease in bacterial population. UV-A and UV-B radiation levels were higher than in previous cases, which positively affect reduction rate.

There might be inaccuracies in the results because of faults in sampling or counting procedure.

6 CONCLUSIONS

It is possible to use solar radiation for water treatment in Finland, but it requires several factors to be aligned, in order to have an efficient process. Sun should shine all treatment time or around 10 hours, which rarely happens in Finland. To increase bacterial reduction water layer depth should not exceed 0,1 m and should be as little as possible to have a faster treatment time. But smaller water layer depth requires larger area of water basin, which increases unit installation costs. Water should be heated to around 40 ^{o}C to satisfy fast and efficient reduction.

It is possible to add some chemical additives in water to provide even faster and more efficient reduction of bacteria. But these chemical additives have to be studied first to ensure that there is no risk on human health and other organisms. Other factors, such as pH level, have to be studied in order to make the process more efficient. Materials that absorb sun light could be used to cover basin bottom to increase water temperature. It is possible to use sunlight concentrators to increase water temperature by solar light, but this would also increase unit costs.

Although it is possible to use solar radiation in water disinfection in Finland, at the moment it is not reasonable, especially for large scale water treatment. Installation costs are too high and treatment process takes too much time. But it can be done for very small scale for personal use in extreme situations. It is important to emphasize that solar disinfection destroys only bacteria and some viruses, but it has little effect on other pollutants found in water. Other pollutants must be removed with other technologies.

REFERENCES

Ajona, J., & Vidal, A. 2000. The Use of CPC Collectors for Detoxification of Contaminated Water: Design, Construction and Preliminary Results. Sol. Energy 68(1), pp. 109-120.

Augugliaro, V., Baiocchi, C., Bianco, A., Brussino, M.C., Garćia-López, E., Loddo, V., Malato, S., Marcí, G., Palmisano, L. & Pramauro, E. 2002. Sunlight Photocatalytic Degradation of Azo-Dyes in Aqueous Suspension of Polycrystalline TiO_2. Fresenius Environ. Bull. 11(8), pp. 459-464.

Bousselmi, L., Geissen, S.U. & Schroeder, H. 2004. Textile Wastewater Treatment and Reuse by Solar Catalysis: Results from a Pilot Plant in Tunisia. Water Sci. Technol. 49(4), pp. 331-337.

Dillert, R., Siemon, U. & Bahnemann, D. 1998. Photocatalytic Disinfection of Municipal Wastewater. Chem. Eng. Technol 21(4), PP. 356-358.

Dillert, R., Vollmer, S., Schober, M., Theurich, J., Bahnemann, D., Arntz, H.-J., Pahlmann, K. & Sager, G. 1999. Photocatalytic Treatment of an Industrial Wastewater in the Double-Skin Sheet Reactor. Chem. Eng. Technol. 22(11), pp. 931-934.

Bahnemann, D. 2000. Current Challenges in Photocatalysis: Improved Photocatalyst and Appropriate Photoreactor Engineering. Res. Chem. Intermed. 262, pp. 207-220.

Herrera, J. A., Doña, J. M., Vieira, A., Tello, E., Valdés, C., Arana, J., and Pérez, J.; 2000, “The Photocatalytic Disinfection of Urban Waste Waters,” Chemosphere, **41**, pp. 323–327.

Herrmann, J.M., Guillard, Ch., Disdier, J., Lehaut, C., Malato, S. & Blanco, J. 2002. New Industrial Titania Photocatalysts for the Solar Detoxification of Water Containing Various Pollutants. Appl. Catal. B 35, pp. 281-294.

Hincapie, M., Maldonado, M.I., Oller, I., Gernjak, W., Sánchez, J.A., Ballesteros, M.M. & Malato, S. 2005. Solar Photocatalytic Degradation and Detoxification of EU Priority Substances. Catal.Today 101, pp. 203-210.

Kurtoglu M. E., Longenbach T., Gogotsi Y. (2011). "Preventing Sodium Poisoning of Photocatalytic TiO2 Films on Glass by Metal Doping". International Journal of Applied Glass Science 2 (2): 108–116.

Malato, S., Blanco, J., Vidal. A., Alarcón, D., Maldonado, M.I., Cáceres, J. & Gernjak, W. 2003. Applied Studies in Solar Photocatalytic Detoxification: An Overview. Sol. Energy 75, pp. 329-336.

Malato, S., Blanco, J., Vidal, A. & Richter, C. 2002. Photocatalysis with Solar Energy at a Pilot-plant Scale: An Overview. Appl. Catal. B 37(1), pp. 1-15.

Rabindranathan, S., Devipriya, S. & Yesodharan, S. 2003. Photocatalytic Degradation of Phosphamidon on Semiconductor Oxides. J. Hazard Mater. 102(2-3), pp. 217-229.

Rincón, A.G. & Pulgarin, C. 2005. Use of Coaxial Photocatalytic Reactor (CAPHORE) in the TiO_2 Photo-Assisted Treatment of Mixed E. coli and Bacillus sp., and Bacterial Community Present in Wastewater. Catal. Today 101, pp. 331-344.

Rossetti, G. H., Albizzati, Enrique D., and. Alfano, O. M., 2004, “Modeling of a Flat-Plate Solar Reactor. Degradation of an Organic Pollutant by thePhoto-Fenton Reaction,” Sol. Energy, **77**, pp. 461–470.

Sano, T., Negishi, N., Takeuchi, K. & Matsuzawa, S. 2004. Degradation of Toluene and Acetaldehyde with Pt-Loaded TiO_2 catalyst and Parabolic Trough Concentrator. Sol. Energy 77, pp. 543-552.

Sarria, V., Péringer, P., Cáceres, J., Blanco, J., Malato, S. & Pulgarin, C. 2004. Solar Degradation of 5-Amino-6-Methyl-2-Benzimidazolone by TiO_2 and Iron(III) Catalyst with H_2O_2 and O_2 as Electron Acceptors. Energy 29, pp. 853-860.

Sattler, C., de Oliveira, L., Tzschirner, M. & Machado, A.E.H. 2004. Solar Photocatalytic Water Detoxification of Paper Mill Effluents. Energy 29, pp. 835-843.

Scott, KJ; Wills, RBH (1973). "Atmospheric pollutants destroyed in an ultra violet scrubber.". *Laboratory Practice* **22**(2): 103–6.

Watanabe, N., Hokoshi, S., Hidaka, H. & Serpone, N. 2005. On The Recalcitrant Nature of the Triazine Ring Species, Cyanuric Acid, to Degradation in Fenton Solutions and in UV-Illuminated TiO_2 (Naked) and Fluorinated TiO_2 Aqueous Suspensions. J. Photochem. Photobiol. A 174, pp. 229-238.

1. Website of Household Energy Network. Referred 21.05.2014. http://www.hedon.info/tiki-index.php
2. Website of Center for International Earth Science Information Network. Referred 21.05.2014. http://www.ciesin.org/
3. Website of Spartan Environmental Technologies. Referred 11.03.2014. http://www.spartanwatertreatment.com/UV-disinfection.html
4. Website of Solar Energy Engineering. Referred 11.03.2014. http://solarenergyengineering.asmedigitalcollection.asme.org/journal.aspx
5. Website of Enviolet. . Referred 09.04.2014. http://www.enviolet.com/en/home.html
6. Website of Home Power. Referred 09.04.2014. http://www.homepower.com/
7. Website of Bio Med Central. Referred 11.03.2014. http://www.biomedcentral.com/
8. Website of Solar Energy Engineering. Referred 11.03.2014. http://solarenergyengineering.asmedigitalcollection.asme.org/journal.aspx

Website of Aquionic News. Referred 09.04.2014.
http://halmapr.com/news/aquionics/

Website of eawag aquatic research. Referred 5.03.2014.
http://www.eawag.ch/index_EN

Website of University of del Valle. Referred 09.04.2014.
http://www.univalle.edu.co/

Website of US Environmental Protection Agency. Referred 11.03.2014.
http://www.epa.gov/

Website of Water School. Referred 18.02.2014. http://www.waterschool.com/

Website of World Health Organization. Referred 5.03.2014.
http://www.who.int/en/